

Natural polymers for emerging technological applications: cellulose, lignin, shellac and silk

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Abstract

In an effort to stave off the growth of electronic waste (e-waste) that poses a critical environmental dilemma, scientists often look into nature as an unending inspirational pool of materials and chemical processes that ensure functionality, performance and safe dissolution at the end of life cycle. This short review highlights only four organic polymer materials of natural origin (i.e. cellulose, lignin, shellac and silk) from the very large pool of natural (bio)polymeric materials and looks not only into the recent developments at the industrial scale but also into the emerging niche applications of these materials, while highlighting their implementation into electronics and sensor development. This review exemplifies that natural polymeric materials have great potential for the development of eco-friendly electronics, in other words the class of industrial products that has carefully considered the important issues of biocompatibility, biodegradability (even compostability), cost of production and energy expanded in production (i.e. the carbon footprint).

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INTRODUCTION

Natural biopolymers, the most abundant organic compounds in the Earth biosphere, are polymers that are freely produced in nature by the cells of living organisms, either plants or animals. They consist of monomeric units that are covalently bonded in linear and branched chains to form larger molecules. According to their chemical structure, the main classes of biopolymers are: (i) nucleic acids (DNA, RNA), (ii) polyamides (proteins and poly(amino acid)s), (iii) polysaccharides (cellulose, starch, natural gums, xanthan), (iv) polyisoprenoids (natural rubber, gutta percha), (v) polyphenols (lignin, humic acids), (vi) organic polyoxoesters (polyhydroxyalkanoic acids, polymalic acids, cutin, shellac), (vii) polythioesters (polymercaptoalkanoic acid, polyhexanedithiol-sebacate) and (viii) inorganic polyesters. Although many of the above-mentioned classes of polymers are actively studied in relation to novel developments in medicine and pharmaceuticals formulations, the present article focuses on the naturally occurring polymers of high-volume availability, i.e. cellulose, lignin, silk and shellac. The interest in biopolymers in the scientific community has risen in the past few years, especially since they are seen as a viable alternative to nonbiodegradable, petroleum-based plastics,^{1–3} the latter group surpassing already the production milestone of 400 million tons/year.^{4,5} It is estimated that ca 8300 million tons of plastic have been produced by mankind since the emergence of the chemical industry, and nearly 6300 million tons of plastic have been discarded into the environment.^{6,7} Considering the important aspect of utilization of a large fraction of plastics for short-term applications only, mankind is still struggling to find appropriate solutions for handling plastic waste. Many of the naturally occurring polymers, or polymers derived from natural sources have the advantage that

they can be digested by bacteria and microorganisms at the end of their life cycle, and are therefore viewed as sustainable platforms that can support the sustainable technological advancement of our civilization.^{1,3} This aspect is crucially important in our modern world where the utilization of energy resources, the carbon footprint and the environmental impact of industrial technologies need careful attention.^{8–10}

With regard to the sustainable development goals of the United Nations,¹¹ it is not responsible and sustainable to continue the polyolefin-based plastic industry on the long run. Therefore, a circular economy is envisioned in the plastic industry, which is very popular and used for regulating the recycling of plastics. On the other hand, it is very difficult to bring in a 100% recycling rate. With each passing day it will be expensive and increasingly more difficult to have a clean environment using polyolefins.

Therefore, it is highly desirable to have materials which are biodegradable and can offer products similar to those produced from petroleum, but with enhanced capabilities. What else is more attractive than biopolymers? Poly(lactic acid) for example is already entering mass production worldwide as a replacement for polyolefins in consumable products, mainly packaging. There are many other biopolymers which can be suitable as substitutes for mass-produced polyolefin-derived polymers. Those materials are clean for nature, due to their biodegradability when discarded

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in the environment. As a result, an accumulation of plastic waste could be curbed by employing such a strategy.

Cellulose, lignin, silk and shellac are examples of biopolymers that have been established as key materials for many industrial-scale applications in different sectors. In this respect, utilization of these biopolymers as textile materials, as bases for novel chemical production, as biomedical materials, as food production ingredients and as other high-value-added products is summarized, with an individual highlight of the employment of each one in the emerging field of bioelectronics.

CELLULOSE AND LIGNIN

The biomass reserves of the Earth have been estimated to be approximately 1.85–2.4 trillion tons and given the increased global concern over the effects of greenhouse gas emission, such biomass has emerged as an abundant and sustainable alternative source of energy and chemicals.¹² The biomass is constituted of three main components: cellulose, hemicellulose and lignin. Cellulose is a natural biopolymer that can be regarded as a linear macromolecular chain of 1,4-linked β -D-glucopyranose, occurring in every cell of all plants on Earth. It is a completely nontoxic, renewable and biodegradable material that exhibits a great chemical variability and can be divided into natural and synthetic cellulose depending on the source of production. Cellulose represents also a massive source material for the fabrication of environmentally friendly and biocompatible products. The production of cellulose from glucose, which itself is produced in plant cells by

the process of photosynthesis, is estimated to be *ca* 1 trillion tons/year, making it the most widely available biopolymer to mankind.¹³ Cellulose is naturally produced not only by all plants on land, but also in the oceans, in the process of fixation of carbon dioxide, as for example in unicellular plankton and algae. The composite material wood is nothing but an outstanding high-strength and durable material composed of cellulose as main component, together with lignin and hemicelluloses (Fig. 1).¹⁴ The composition of some well-known sources of natural cellulose is presented in Table 1,^{15,16} which shows that the two major sources of natural cellulose are wood and cotton, both having a chemical composition depicted as cellulose I in Fig. 2.¹⁷

Some prominent players in the global cellulose market include: Weyerhaeuser Company, Honeywell International, DuPont de Nemours, Inc., Invista, Daicel Corporation, Nylstar, Zhejiang Fulida, Lenzing, Fiber Visions Products and Eastman Chemical, with many more trading companies in the world involved in handling cellulose products.

However, despite the usage of cellulose for millennia by mankind as energy source and in clothes production, the employment of pure cellulose in high-added-value applications is sporadic, due in part to its insolubility in water as well as in most organic solvents, its hygroscopic character and its inability to melt without decomposition. As a consequence, synthetic nanocellulose has attracted increased attention in recent years, due to its customizable chemical and physical properties of the material that suit various applications. In effect, the worldwide production of cellulose fibers (including here the above mentioned synthetic

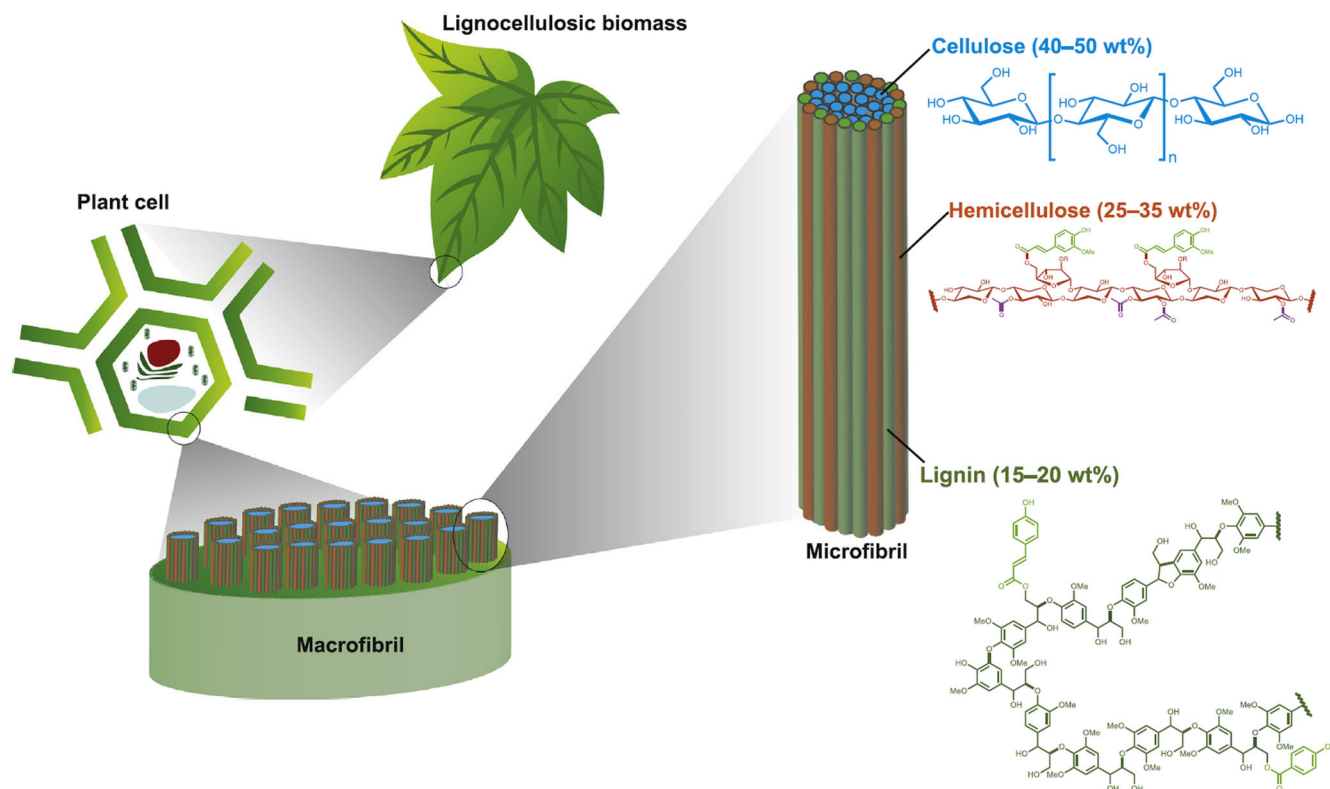


Figure 1. Descriptive presentation of the structure of lignocellulosic biomass and its three main constituents: cellulose that accounts for *ca* 40–50 wt% of the biomass is a linear homopolymer of glucose linked through β -1,4-glycosidic bonds; hemicellulose that accounts for *ca* 25–35 wt% of the biomass is a heteropolymer of C₅ and C₆ sugars linked through different glycosidic bonds; and lignin that accounts for *ca* 15–20 wt% of the biomass is an aromatic heteropolymer comprising various phenylpropanoid units. Fibrils of cellulose surrounded by hemicellulose and lignin constitute the microfibrils that bundle together in macrofibrils, which represent the main component of the cell walls of plants. Reproduced with permission from Ref. 14.

Table 1. Chemical composition some plants of industrial relevance. Reproduced from Ref. 16

Source	Composition (%)			
	Cellulose	Hemicellulose	Lignin	Extract
Hardwood	43–47	25–35	16–24	2–8
Softwood	40–44	25–29	25–31	1–5
Bagasse	40	30	20	10
Coir	32–43	10–20	43–49	4
Corn cobs	45	35	15	5
Corn stalks	35	25	35	5
Cotton	95	2	1	0.4
Flax (retted)	71	21	2	6
Flax (unretted)	63	12	3	13
Hemp	70	22	6	2
Henequen	78	4–8	13	4
Istle	73	4–8	17	2
Jute	71	14	13	2
Kenaf	36	21	18	2
Ramie	76	17	1	6
Sisa	73	14	11	2
Sunn	80	10	6	3
Wheat straw	30	50	15	5

nanocellulose) amounts to 7.3 million tons/year,¹⁸ with the main industries handling cellulosic fibers being aerospace and defense, automotive, paper and pulp, construction, electrical/insulation, textile and fireproofing. In the class of synthetic nanocellulose (with particle sizes of between 1 and 100 nm), one can distinguish two products depending on the fabrication route, i.e. cellulose nanocrystals (CNC), which are obtained by acid treatment, and cellulose nanofibrils (CNF), obtained by mechanical disintegration. Crystalline cellulose depicted as cellulose II in Fig. 2 is an important industrial product since it represents the precursor of viscose, as well as various cellulose esters and ethers.

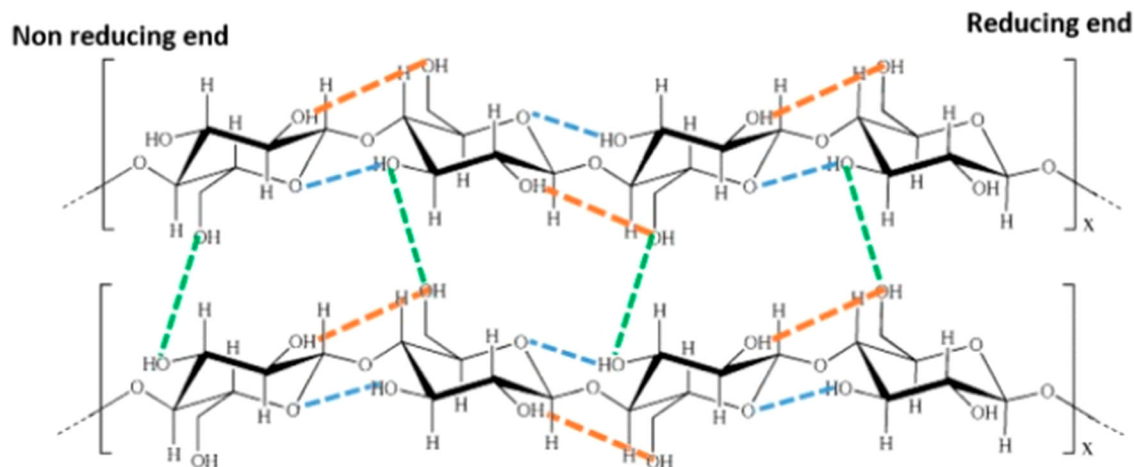
The fabrication of CNF takes place in sequential operations, depicted schematically in Fig. 3.¹⁹ Because of the exhaustive steps necessary to obtain the refined final product, the process of carbon nanofibril production is difficult to be scaled up to the level of industrialization. In addition, lowering the amount of energy expended in the process remains a formidable obstacle.

In addition to being extracted from wood and plants, nanocellulose can be synthesized by bacteria (i.e. bacterial cellulose, BC) and by electrospinning cellulose nanofibers (i.e. ECNF). Among the four types of nanocellulose, CNC and CNF have a wider industrial relevance since their fabrications are regarded as top-down processes, being produced by disintegration of cellulose fibers into nanoscale particles. BC and ECNF production on the other hand are bottom-up processes, generated by a buildup of nanofibers from low-molecular-weight sugars by bacteria (Fig. 4) or from dissolved cellulose by electrospinning, respectively. The assembly of cellulose nanofibers by bacteria involves two steps, illustrated schematically in Fig. 4: (i) the assembly of cellulose molecules extruded from the same extrusion pore into a single elementary nanofiber with a diameter of *ca* 1.5 nm and (ii) the congregation of multiple elementary nanofibers into a ribbon-like nanofiber of 3–4 nm in thickness and 70–80 nm in width in the cross-section, which is further woven into a three-dimensional network with the appearance of a pellicle floating at the surface of culture media.^{20,21} BC has unique structural and mechanical properties

that differentiate it from wood- or plant-derived cellulose. In this respect, the purity of BC is much higher than that associated with plant-based cellulose because the fewer steps necessary for production are translated in a final product devoid of polymer contaminants, which is unfortunately a characteristic of the latter cellulose type.²² Moreover the degree of crystallinity of BC is much higher than that of plant-based cellulose, with a value approaching 90%.²³ The water retention of BC is outstanding, given by the fact that the hydroxyl groups in the glucose units can interact efficiently with water molecules, leading to *ca* 90% water retention capability. The advantageous mechanical properties of BC, coupled with its biocompatibility, nontoxicity, formability, softness, cost-effectiveness and ability to be derived synthetically to incorporate secondary components, such as antibiotics, into its pores, have led to BC as the candidate of choice for many applications on human tissue, like for example plasters for wound healing (Fig. 4).²¹

The usage of cellulose in electronics applications is not yet established industrially, despite recent reports in the literature that take advantage of the unique film-forming and outstanding dielectric properties of cellulose.^{24–30} Advantageously, nanocellulose can be patterned photolithographically, opening in this way the avenue for practical industrial exploitation in the electronics field.³¹ In a recent report, trimethylsilyl-derivatized nanocellulose (TSMC) synthesized in ionic liquids³² was employed as robust dielectric for high-performance organic field effect transistors (OFETs) and complementary inverters²⁴ (Fig. 5). Panels (a)–(e) in the red frame of the Fig. 5 present the robust dielectric properties of TSMC, which functions either as a stand-alone insulator or as a thin capping layer for an inorganic aluminium oxide dielectric. The high purity of the synthesized material is translated into a relatively flat capacitance over a wide frequency window spanning from kHz to MHz, and a loss angle always lower than 0.1 which is a remarkable behavior, as demonstrated in panel (e). The breakdown field of 4.4 MV cm⁻¹ extracted from the measurement shown in panel (d) compares favorably with synthetic polymers

CELLULOSE I



CELLULOSE II

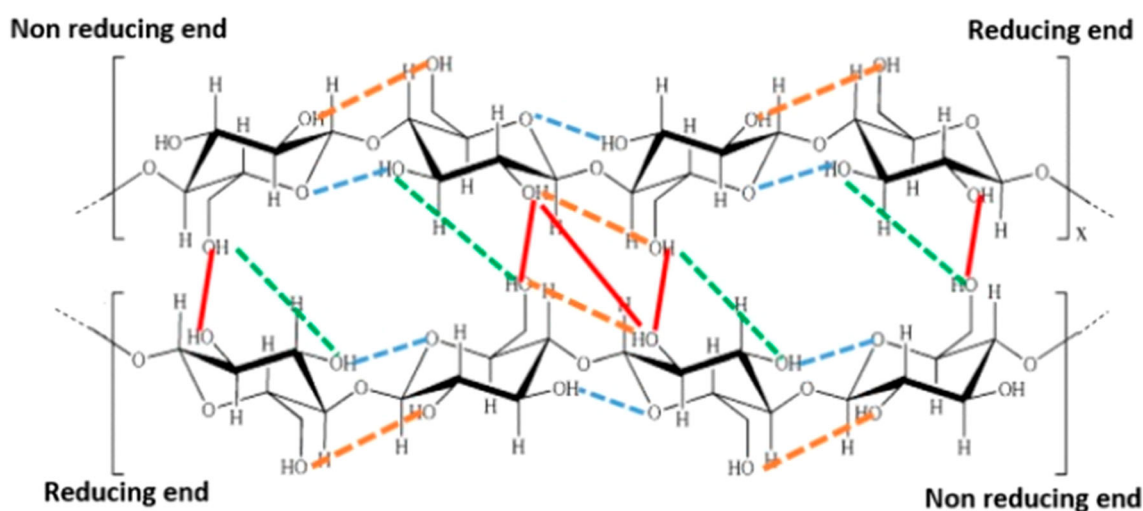


Figure 2. Intermolecular and intramolecular hydrogen bonds in the two allomorph structures of cellulose, cellulose I and cellulose II: intramolecular 2 (OH)...O-6 (orange dash lines), intramolecular O(3)H-O pyranosidic (blue dash lines), intermolecular O(6)H-O(30) (green dash lines) and intermolecular O(2)H-O(2) and O(6)H-O(20) (red solid lines). Reproduced with permission from Ref. 17.

like benzocyclobutene whose breakdown field was reported as being 4.5 MV cm^{-1} .^{33,34} Panels (a)–(d) in the blue frame of Fig. 5 show the outstanding dielectric behavior of TMSC employed as capping layer for inorganic dielectric aluminium oxide. Both the transfer and output characteristics are virtually hysteresis free and the OFETs display a minimal leakage current in the range of nA throughout the measurement window. Perhaps the most outstanding role of TMSC is displayed in the complementary inverters fabricated with pentacene and fullerene C_{60} , shown in panels (a)–(c) in the green frame of Fig. 5. In this respect, world record values of static gain in excess of 1000 V V^{-1} were recorded (with record values up to 1600 V V^{-1}). In addition, the inverters displayed a world best value of noise margin of 92.5% at a supply voltage of 4 V, which surpasses all the previous reports concerning other combinations of dielectrics and semiconductors.³⁵ Interestingly, TSMC film can be transformed into pure cellulose by

vapor-phase acid hydrolysis (i.e. desilylation) through a simple exposure for 90 s to vapor of 2.5 mol L^{-1} hydrochloric acid solution. The process involves a reduction of the film thickness by about 70% that affects nonetheless the quality of the film surface. Nevertheless, the noise margin of the complementary inverters fabricated with regenerated cellulose film via the desilylation method still displays an exceptional value of 82% at 2.5 V operating voltage.²⁵

Lignin is the second most accessible biopolymer to mankind after cellulose, with an estimated immediate availability of ca 100 million tons/year, being in fact an undesired byproduct of the paper and pulp as well as cellulose production industries.³⁶ It is worth pointing out that in reality lignin is not the second most widespread biopolymer produced by nature, that being chitin with a total steady-state availability in nature estimated to come close to 100 billion tons as part of the shells of living organisms

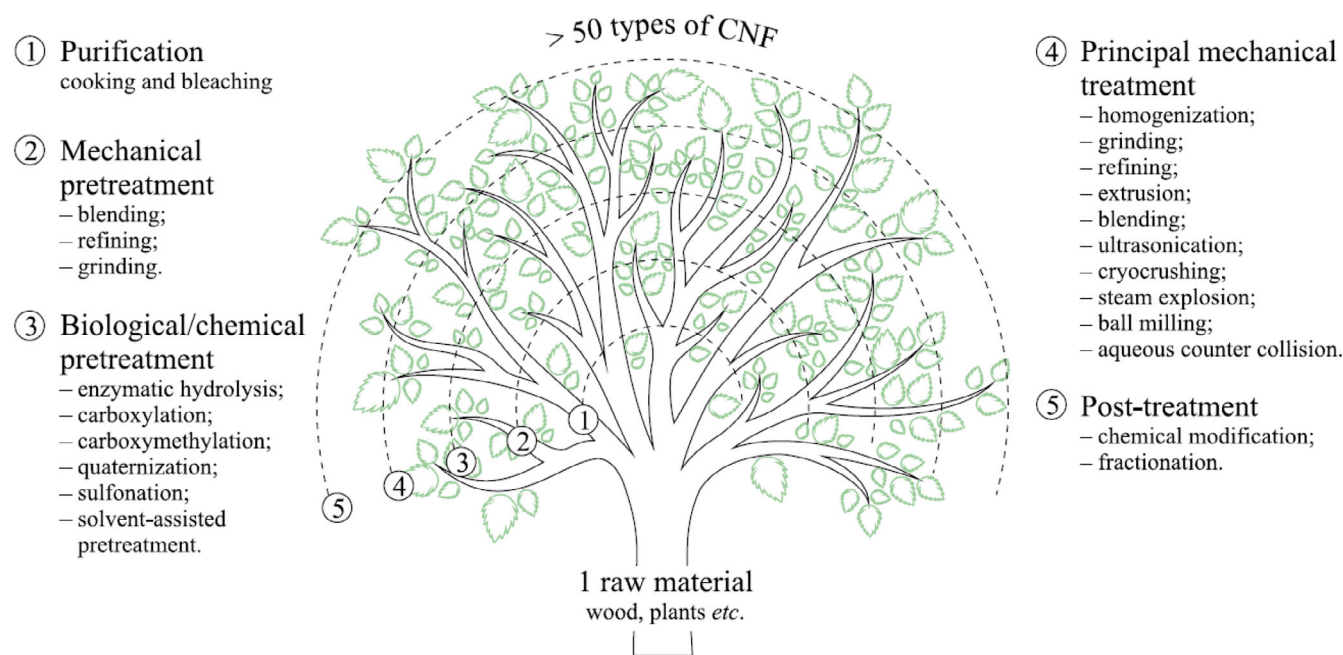


Figure 3. Schematic diagram of the fabrication sequence of more than 50 types of CNF. Reproduced with permission from Ref. 19.

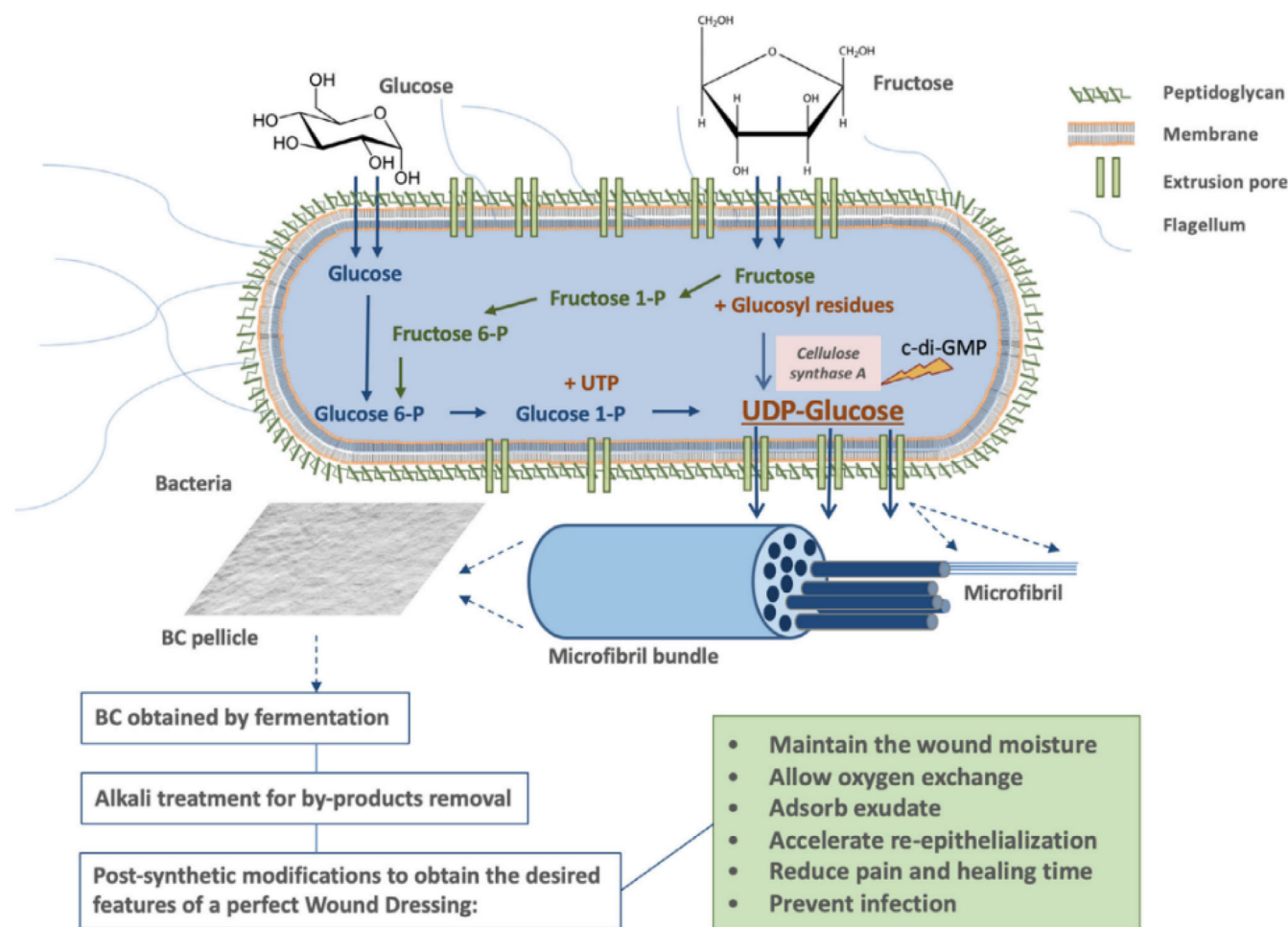


Figure 4. Schematic representation of the steps involved in the production of a BC-based wound healing material. Reproduced with permission from Ref. 21.

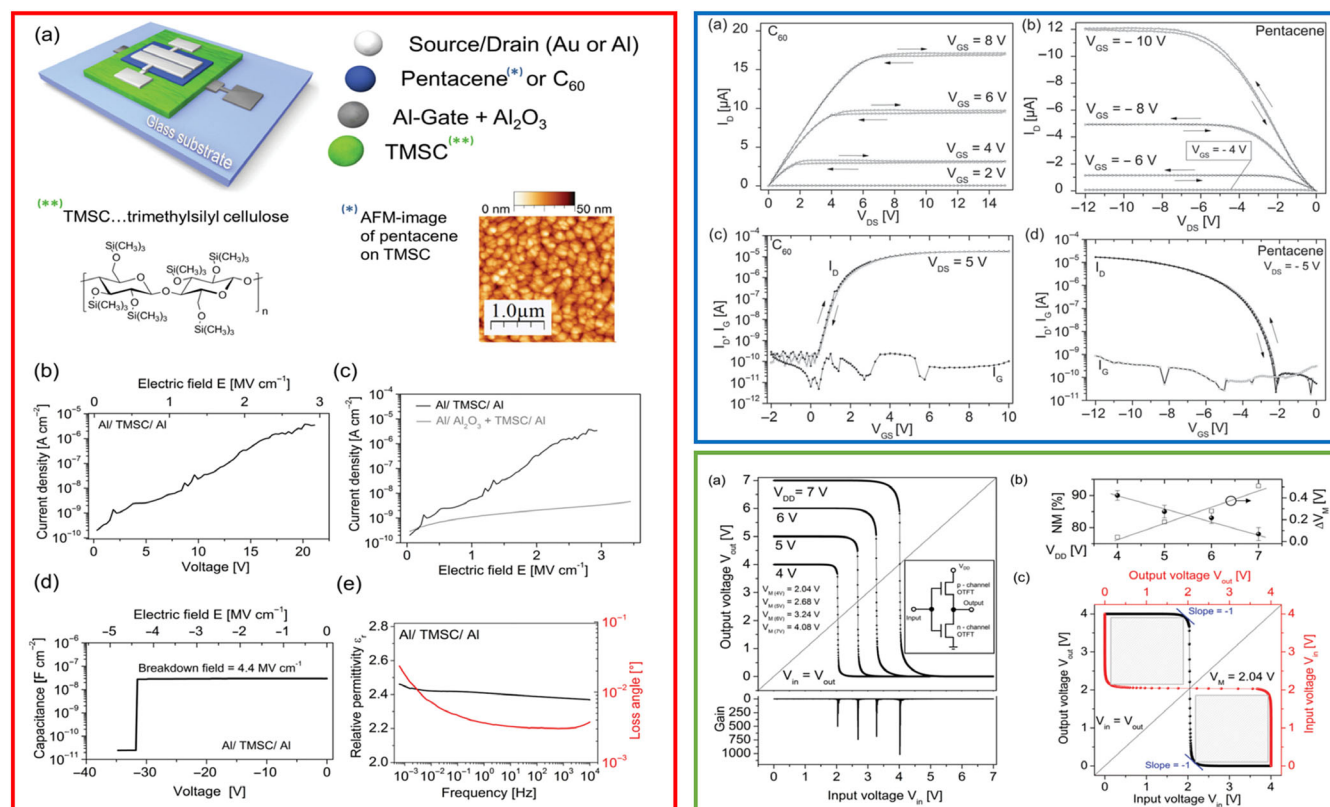


Figure 5. Red frame: (a) Schematic of fabricated OTFTs, containing glass substrate (light blue), aluminium gate electrode (gray), TMSC dielectric layer (green), organic semiconductor (pentacene or C_{60}) (navy blue) and source and drain electrodes (Au or Al) (gray). The insets show the chemical structure of TMSC and an AFM image of pentacene on TMSC. (b) Example of electrical measurements of a metal–insulator–metal in sandwich sequence Al/TMSC/Al with an overlapping electrode area of 0.1 cm^2 and a TMSC layer thickness of 72 nm , showing the current density curve. (c) Current density curve in comparison to a bilayer inorganic–organic dielectric of $28 \text{ nm Al}_2\text{O}_3$ and 30 nm TMSC . (d) Capacitance versus voltage displaying also the breakdown field of an Al/TMSC/Al sandwich structure. (e) Dielectric permittivity (left axis) versus frequency and loss angle (right axis) versus frequency curves of a capacitor with a single layer of TMSC. Blue frame: Examples of transistor characteristics of C_{60} - and pentacene-based OFETs with channel length $L = 25 \mu\text{m}$ and channel width $W = 2 \text{ mm}$ on a combination dielectric consisting of $28 \text{ nm Al}_2\text{O}_3$ and $25\text{--}30 \text{ nm TMSC}$. Output and transfer characteristics of (a, c) C_{60} and (b, d) pentacene OFETs. Green frame: (a) Voltage transfer characteristics (VTCs) and inverter gains of a complementary inverter structure for supply voltages between 4 and 7 V . The inset presents the circuit schematic of the complementary inverter. (b) Noise margin (NM) and mismatch ΔV_M of the threshold voltage V_M as a function of the supply voltage, with the error bars of the NM also displayed. (c) Determination of the NM at $V_{DD} = 4 \text{ V}$ using the ‘maximum equal criterion’ by finding the maximum size of a square that fits between the inverter curve and the mirrored inverter curve. Reproduced with permission from Ref. 24.

(i.e. freshwater and saltwater arthropods). Nevertheless, to date chitin has found no large-scale industrial applications, other than being the precursor of chitosan, with the latter production in the range of 4000 tons/year . Lignin on the other hand is available in the amount mentioned above and its total value is estimated to surpass $\$900 \text{ million}$ by 2025 .³⁶ Lignin has attracted recently increased interest for a plethora of industrial applications that will be enumerated in the following. Lignin is the biopolymer that is responsible for the overall rigidity of cell walls and is generated in nature during radical coupling of phenylpropanoid units, such as *p*-coumaryl, coniferyl and sinapyl monolignols. Chemically, lignin can be regarded as a polyaromatic macromolecule and can be divided into two categories, sulfur-containing and sulfur-free lignin, as shown in Fig. 6. Among the listed types of lignins, the most prominent globally are the lignosulfonates (*ca* 88%), followed by kraft lignins (*ca* 9%). Nevertheless, an emerging category is represented by the organosolv lignins with a prominence of *ca* 2% globally especially since it is employed in the production of bioethanol. However, the production of lignin far surpasses the demand for its use as a fuel, either to be burnt directly with a significantly lower efficiency than petroleum per kilogram or as a

precursor for bioethanol production. Therefore, increased attention has been given recently to lignin valorization and to enlarging the market for lignin applications.

The process of valorization of lignin requires that the biopolymer be separated from cellulose, and several such industrial processes are presented in Fig. 7. Depending on the catalyst employed in the separation process, different reactive intermediates can be formed on the lignin backbone and these intermediates can then experience further reactions either with other lignin units or with chemicals present in solution. The two most common and well-known methods for the industrial extraction of lignin are the kraft (black pathway in Fig. 7)³⁷ and the sulfite (light-blue + gray pathway in Fig. 7)³⁷ processes, with the processes having been described in detail elsewhere.¹⁴ Both processes involve aqueous solutions for the extraction of lignin from the lignocellulosic mixture. However, novel methods of extraction make use of organic solvents and process temperatures up to $250 \text{ }^\circ\text{C}$ in order to fractionate the biomass.³⁸ These methods are coupled under the organosolv lignin pathway (red pathway in Fig. 7). An ultimate improvement to the process of lignin extraction involves the addition of aldehydes such as formaldehyde to the acid-

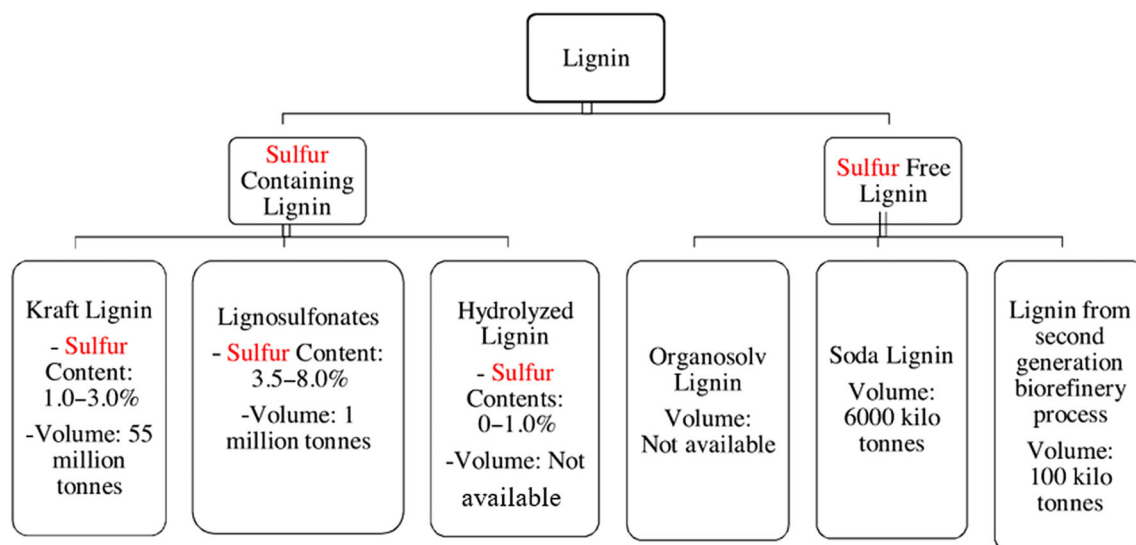


Figure 6. Various types of lignin and their current volumes on the world market. Reproduced with permission from Ref. 36.

catalyzed organosolv process, which substantially improves the quality of the final product (blue pathway in Fig. 7).³⁹

Table 2 presents the main material categories derived from lignin, the reported products and their practical applications. However, in recent years, several other emerging applications have been reported for lignin in different fields.³⁶ In this respect, lignin is intensively studied for its depolymerization pathways, synthesis of chemically active sites, functionalization of hydroxyl groups and production of lignin graft copolymers. Among the novel materials and compounds derived from lignin are lignin-based carbon fibers, phenolic materials, oxidized compounds, hydrocarbon compounds, urethanes and epoxy resins, fire retardants and antioxidants, lignin-derived sequestering agents and lignin-based nanomaterials.^{40–44} Emerging applications (although being currently in the stage of proof of concept) are in the biomedical and energy storage fields. In the biomedical field, lignin has found applications as microcarrier capsules on which many valuable therapeutic agents could be physically attached or encapsulated. In this respect, lignin nanotubes and lignin nanowires are proposed as vehicles for the delivery of DNA and therapeutic agents.⁴⁵ In addition, active research is underway in the areas of tissue engineering, immunomodulation, anticancer and antimicrobial hydrogel formulations based on lignin molecules.^{46–48} In the energy storage field, lignin has found many usages in various components of batteries and supercapacitors aimed at not only improving efficiency but also reducing toxicity, and creating a more cost-effective and sustainable (ecological) product.^{49–51}

Lignin demonstrated recently its suitability for the development of sustainable OFETs.⁵² However, that report remains isolated in the electronics field and requires significant attention in order to reach the level of industrial interest. Figure 8 presents the output and transfer characteristics of kraft lignin acting as a stand-alone dielectric on plain aluminium gate with both C₆₀ (Fig. 8(a),(b)) and pentacene (Fig. 8(c),(d)) semiconductors.

The major problem remaining to be solved is the limited solubility of lignin in organic solvents. As a report demonstrated,⁵² the alternative method of solubilizing lignin in ionic-rich liquids (i.e. alcohol–ammonia mixtures) has the undesired effect of trapping mobile ions in the dielectric film of lignin, which are

subsequently responsible for the occurrence of hysteresis effects in transistor characteristics.^{53,54}

SHELLAC AND SILK

Shellac and silk are both biopolymers of animal origin with a long history in production, trade and development. They are arguably the only two biopolymers of animal origin in the world that have at the present time an industrial significance, with production volumes in thousands of metric tons per year.

Silk production, textile weaving and textile trade represented a milestone in the development and advancement of human civilization on Earth, with historic Chinese reports documenting silk commerce as early as 2700 BC.^{55,56} Silk originates from various insect and spider species (e.g. silkworms, spiders, flies and silverfish) and is composed of two different proteins, sericin and fibroin, among which the latter is an FDA-approved material for some medical applications. Silk fibroin has in fact a large spectrum of applications, including the textile industry, biomedicine, catalysis and many more. Each silk-producing insect and spider species produces silk of a particular amino acid composition, which gives the silk particular mechanical properties.⁵⁷ Among the known silks, spider silk has a highest tensile strength, extensibility and toughness; however, such silk does not have an industrial significance due mostly to limited availability. Mulberry worm silks are the ones commonly employed for textiles manufacturing and biomedical applications, with the total market of silk surpassing 200 000 metric tons in 2016^{58,59} that represented a world record. Although many countries in the world are specialized in silk production stemming from mulberry silkworms, India and China share ca 98% of the global silk market. Among the companies acting as top players in the world, one can name China Silk, Silk Road Holding Group, Jiangsu Huajia Silk, Guangdong Silk-Tex Group, Jai Textart, Garimaa Silks, Guangxi Jialian Silk, Zhejiang Jiaxin Silk, Mianyang Tianhong Silk, Guangxi Guihe group, Jiangsu Xinyuan Silk, Jiangsu Soho International, Guangxi Huahong Silk and Zhejiang Cathaya International.

Structurally, silk contains about 75% of a triangular cross-sectional shape fiber called fibroin and about 25% of gum in a

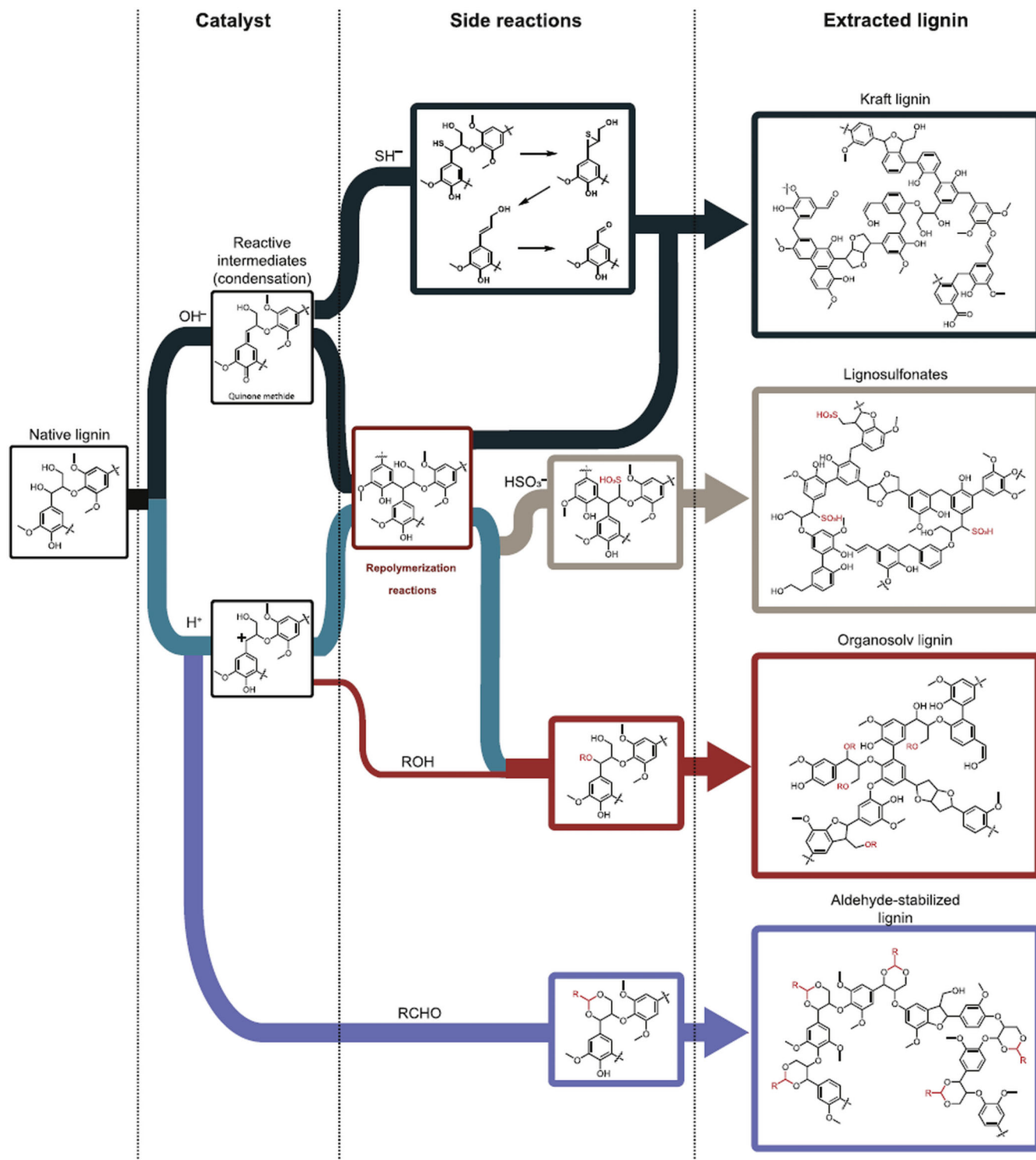


Figure 7. Typical methods for lignin isolation and its subsequent chemical modifications. The kraft process (top pathway, black line); the sulfite process (light-blue/gray pathway); aldehyde-stabilized lignin (bottom pathway, navy blue). The proposed final structures of extracted lignins resulting from all of these reaction pathways are displayed on the right. Reproduced with permission from Ref. 14.

form of a globular protein called sericin.⁶⁰ The sericin protein coats the fibroin fiber and acts as a protective layer. The production of natural silk fiber from farm and wild silkworms is presented in Fig. 9. The process of secreting the natural silk fiber by the silk caterpillar occurs at a rate of 25 cm min^{-1} , and the cocoon itself is formed of a single fiber that approaches 3 km in length. The

processing of the silk involves immersion of the cocoons in hot water to soften the sericin and allow unwinding of the fiber and intertwining it with other fibers in separate yarns.⁶⁰

The mechanical properties of natural silk fibers are simply astonishing, placing them in the range of materials representative of every high-end synthetic fiber or wire, shown

Table 2. Lignin-derived material categories, functional products and their proposed applications. Adapted and reproduced with permission from Ref. 36

Material category	Lignin type	Products	Potential applications
Aromatic macromolecules and fine chemicals	Klason, kraft, organosolv	Lignin monomers and dimers, aromatic phenols, alkyl phenols, aromatic aldehydes, aromatic alcohols, acids, aryl ketones, antioxidants, dispersants, polyurethanes, phenolic resins, vanillin	Industrial chemicals, biobased adhesives, multifunctional materials, building blocks for biobased products
Carbon materials, biofuels	Kraft, sulfite, soda, organosolv	Biochar, bio-oil, syngas, activated carbon, carbon fibers, carbon black	Lightweight polymer composites, adsorbents, electrochemical devices, automobiles
Polymer and nanomaterials	Kraft lignin, organosolv, straw lignin	3D printing resin (cationic surfactant), scaffolds, lignin nanotubes, hydrogels, lignin nanotubes	Biomedical applications, tissue engineering, drug delivery
Energy storage	Kraft lignin, Klason	Li-ion, Na-ion batteries (electrodes), supercapacitors, solar cells	Energy devices, batteries, fuel cells
Building materials	Kraft lignin, Klason	Bitumen, cement additive, dispersant, reinforcement	Construction pavements, cement panels
Specialized applications	Kraft, sulfite, soda, organosolv	Soil conditioner, controlled release agent in fertilizers and pesticides, sequestering agent, contaminant absorbent, fire retardant	Agriculture, textiles, soil reclamation, water purification, fire suppression

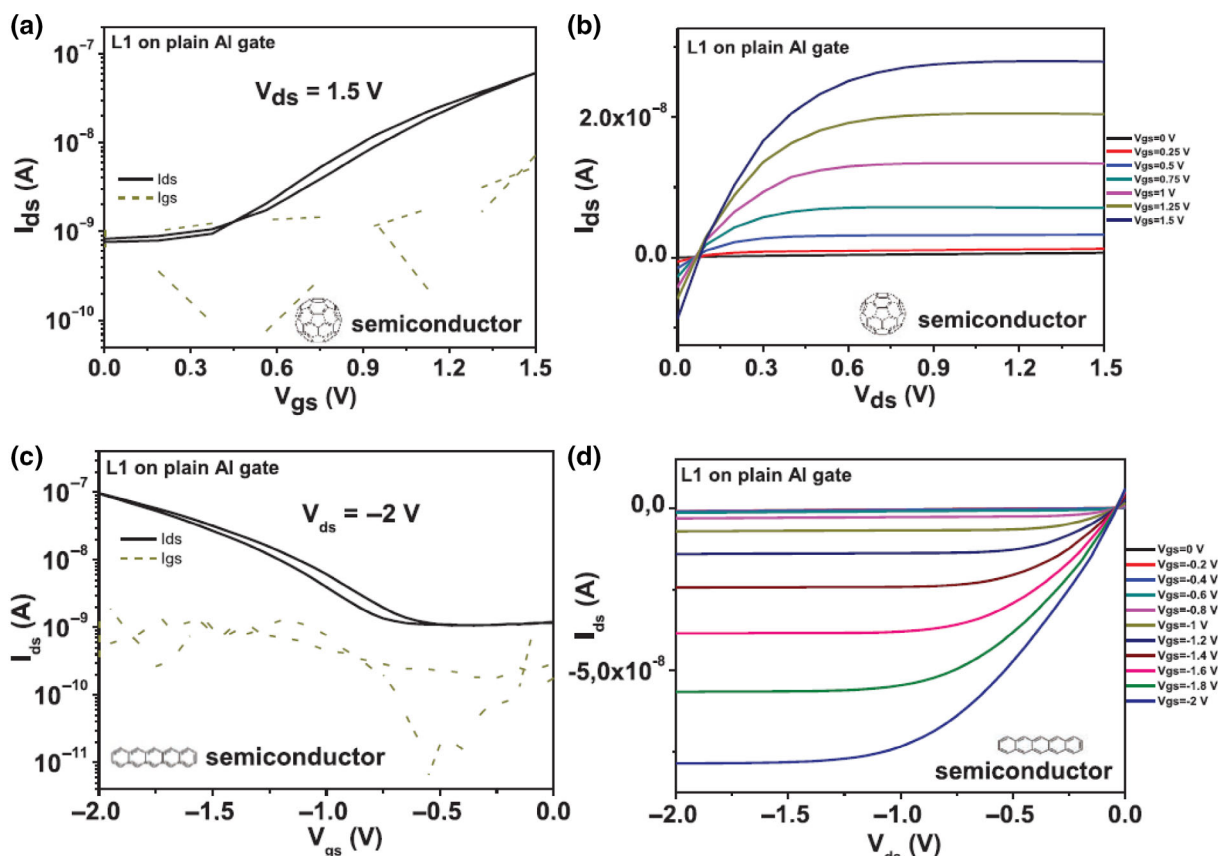


Figure 8. Transfer and output characteristics of kraft lignin solubilized in a mixture of methanol and ammonia, and deposited via doctor blading on plain aluminium gate electrode for OFETs: (a, b) fullerene, C_{60} , semiconductor; (c, d) pentacene semiconductor. Reproduced with permission from Ref. 52.

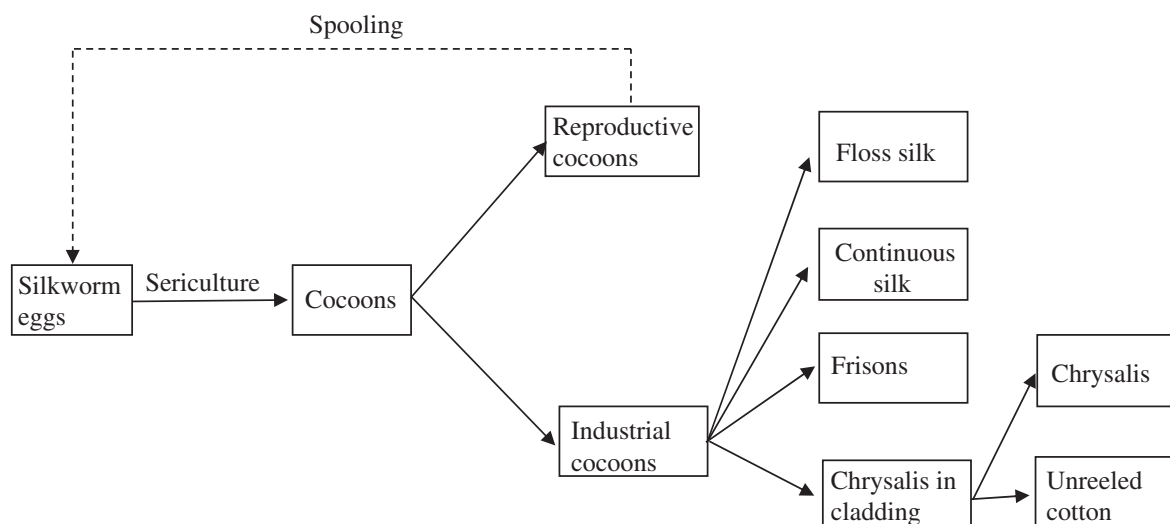


Figure 9. Flow chart of natural silk production. Reproduced with permission from Ref. 60

descriptively in Fig. 10.⁶¹ In terms of strength-to-weight ratio it is important to keep in mind that the spider silk strength of *ca* 1.1 GPa is similar to that of high-tensile engineering steel (i.e. *ca* 1.3 GPa), while the former has a relative density of *ca* 1.3 compared to that of the latter of *ca* 7.8, when reeled at 20 mm s^{-1} at $25 \text{ }^\circ\text{C}$. At the same time, the toughness of spider silk is $ca 165 \pm 30 \text{ kJ kg}^{-1}$, which is substantially higher than that of polyaramid fiber Kevlar 81 (*ca* 33 kJ kg^{-1}). Drawing the silk fiber from the *Bombyx mori* silkworm at different speeds has the advantage of allowing the control of fiber mechanical properties, and generates fibers of desired properties that can be tailored according to the desired application (Fig. 10(b)). Figure 10 (c),(d) shows the mechanical properties of spider silk in comparison to the respective values of other known materials, either natural or synthetic.

Although the global market of silk is predominated by its fiber application for textile manufacturing, silk has emerged recently as a material of choice for a plethora of other applications, schematically exemplified in Fig. 11.

Figure 11 presents the two possible avenues of silk implementation in novel technological applications: one including natural silk and the other involving genetically engineered silk. Genetically engineered silk has the advantage of precise control exercised by the designer over the mechanical, morphological and structural features of silk, which can be used to generate novel material forms and platforms for a wide range of applications. Natural silk sutures are nowadays replaced by other degradable polymer system-based fibers (most notably poly(lactic acid) and poly(lactic-co-glycolic acid)); however, silk sutures are still used for eye and lip surgery, intraoral surgery and for some skin wounds. Other medical applications of silk exemplified in Fig. 11 comprise drug delivery systems, and fiber-based products for ligament, bone and tissue repairs. Emerging applications for silks are in the areas of environmentally compatible systems; photonics (as implantable optical systems for diagnosis and treatment); as well as electronics (as transient substrates for flexible, conformable, implantable, biodegradable and even resorbable electronic displays for improved physiological recording).^{62,63}

In the area of electronics, we highlight in this short review the usage of silk as an organic dielectric material for field effect

transistors.^{64–69} Not surprisingly, the bulk of the work on silk as a dielectric material for OFET and organic light-emitting transistor fabrication originates from research groups in Asia, having as incentive the desire to find new markets and applications for silk. Figure 12 demonstrates that by employing a thin interfacial layer between the organic semiconductor and silk, i.e. 2 nm of pentacene, the growth of C_{60} in larger grain sizes is largely favored, which translates in an increase of the drain current by almost two orders of magnitude, i.e. from 8.5×10^{-7} to $4.5 \times 10^{-5} \text{ A}$ and an afferent improvement of field effect mobility by two orders of magnitude, from 0.014 to $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁶⁴ As a matter of fact, in recent years many reports have emerged concerning the application of silk in advanced technological applications, i.e. photonics, thin-film and conformal electronics, field effect transistors and light-emitting transistors. These advances set the stage for the fabrication of eco-friendly, sustainable and bioactive electronic devices. The advantages of the substrate properties of this all-natural biopolymer can be exploited as an alternative to rigid substrates, enabling the fabrication of degradable devices at a controlled biodegradation/dissolution rate,^{70–72} opening in this way a viable pathway for sustainable high-tech manufacturing.

If silk is a material known since as early as 2700 BC,^{55,56} shellac is itself an engineering material known for several millennia. Shellac was as a matter of fact mentioned even in Mahabharata, the revered Indian novel written in verses that was completed during a period between 400 BC and AD 400. In this respect, shellac can be considered the first material reported in a written publication. In the Mahabharata incidence, an Indian prince offers to a beloved wife a residence palace fully varnished with shellac. This particular utilization of shellac remained over the centuries its major application, with shellac-producing centers scattered in the south and the center of the Asian continent, i.e. India, Thailand, China, Myanmar and Bangladesh. Several companies are involved worldwide in shellac production and trading; however, there is only one company in the world, i.e. AF Suter, with its branches in India, Germany and UK, that oversees the entire industrial process, i.e. harvesting, processing and commercialization of various custom-made applications. Major markets of shellac are varnish formulations for woods, coating (glazing) for pharmaceutical drugs (mainly as barrier coating, enteric coating and taste masking for

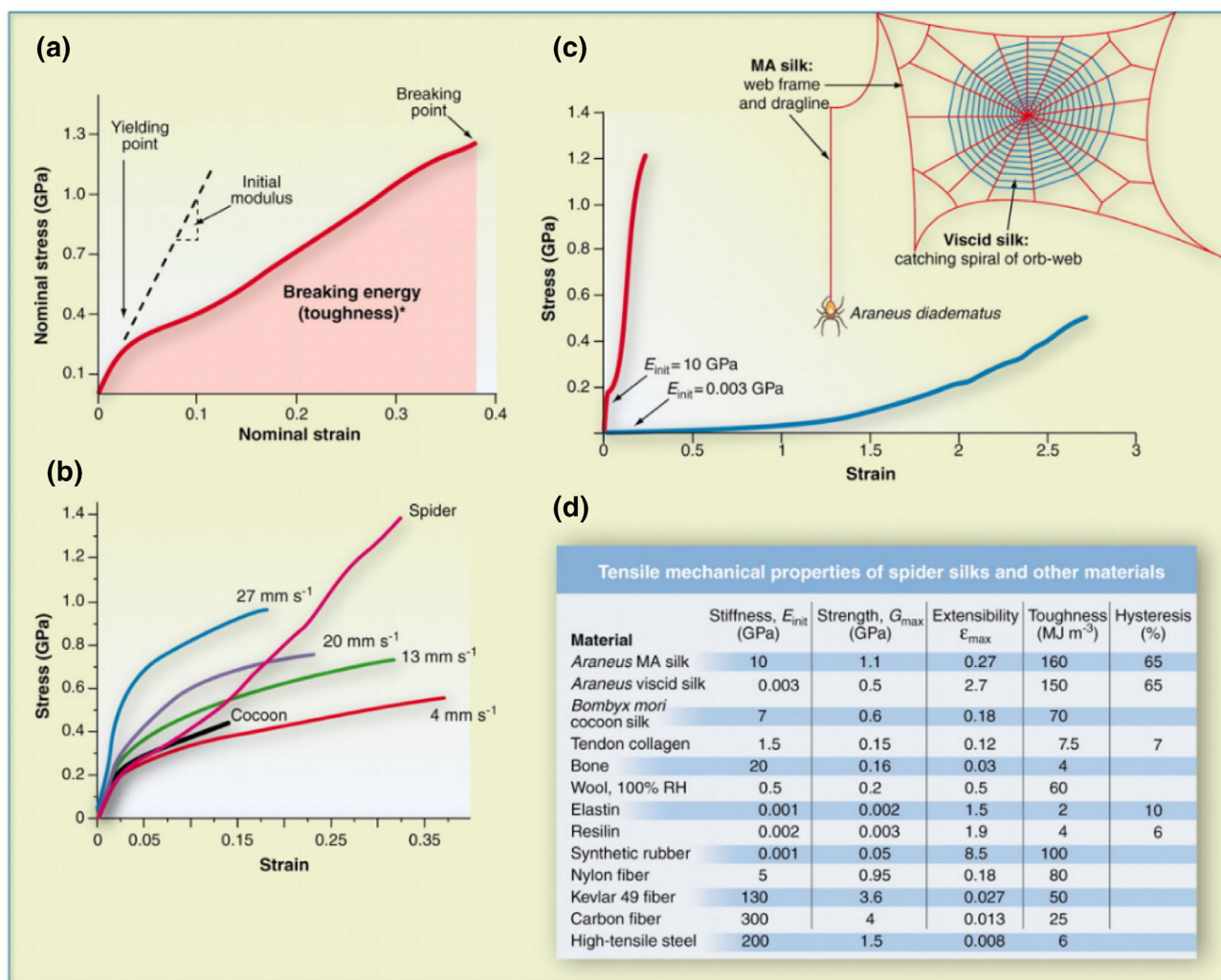


Figure 10. Mechanical properties of silks. (a) Toughness (energy taken up by the material before breaking) and relative tensile strength (maximum stress that a material can withstand while being stretched or pulled before breaking) of reeled spider dragline silk. (b) Comparison of the stress–strain curve of spider silk and silkworm silk from *Bombyx mori* caterpillar obtained at different drawing speeds. (c) Stress versus strain curves for major ampullate (MA) gland silk (red line) and viscid silk (blue line) from the spider *A. diadematus*. E_{init} stands for initial stiffness. (d) Tabulated data from multiple sources and based on data from the spider *A. diadematus*. Reproduced with permission from Ref. 61.

bitter pills) and coating barrier for the prevention of moisture release for citrus fruits, where shellac is given the food ingredient number E 904 in the European Union. Additionally, shellac is a gastro-resistant polymer which means it provides protection at lower pH levels (in the stomach) but dissolves at higher pH in the small intestine, hence its prominent usage as an enteric coating material. In total, the amount of shellac commercialized in the world exceeds 20 000 tons/year, and importantly it is wholly a natural product; there is no synthetic alternative to shellac in the world.

Shellac biopolymer is laid on the branches of host trees by the female lac bug, a minuscule insect of 0.5 mm in size that lives in colonies on the branches of host trees. Among the most common lac insects are *Kerria lacca* and *Kerria chinensis* and their preferred host trees that support the growth of colonies are: kusum (*Schleichera oleosa*), dhak (*Butea monosperma*) and ber (*Ziziphus mauritiana*) in India, rain tree (*Albizia saman*) in Thailand and pigeon pea (*Cajanus cajan*) in both China and Thailand. In addition to these tree species, also various *Hibiscus* tree species support the growth of shellac-laying insect colonies. Among the above-mentioned

trees, the kusum tree is the one that is recognized to give the highest yield along with low base color levels of shellac.⁷³ The explanation for the difference in yield is given by the life cycle of the lac insect, which feeds on the sap of the tree (therefore the preference for a specific tree), produces shellac as part of its own metabolism and secretes it on the branches of the trees as encrustation. The deposit acts as a source of food for the larvae immediately after their emergence from the laid eggs, and offers at the same time housing, i.e. protection to the strong UV radiation experienced in certain areas of the globe. Given the multiple possibilities (tree species and strains of insects), the final shellac product comes in a multitude of colors and intricate compositions. The encrustation deposited by lac insects represents the original biopolymer, known in shellac nomenclature as sticklac. It is crudely purified directly at the producers by cleaning it from impurities and then solubilizing it in water in order to remove the water-soluble anthraquinone derivatives in the form of laccic acids (colorants). The removal of the red colorant produces the next shellac product known as seedlac. The remaining brownish color of the seedlac can be further reduced in various processing steps

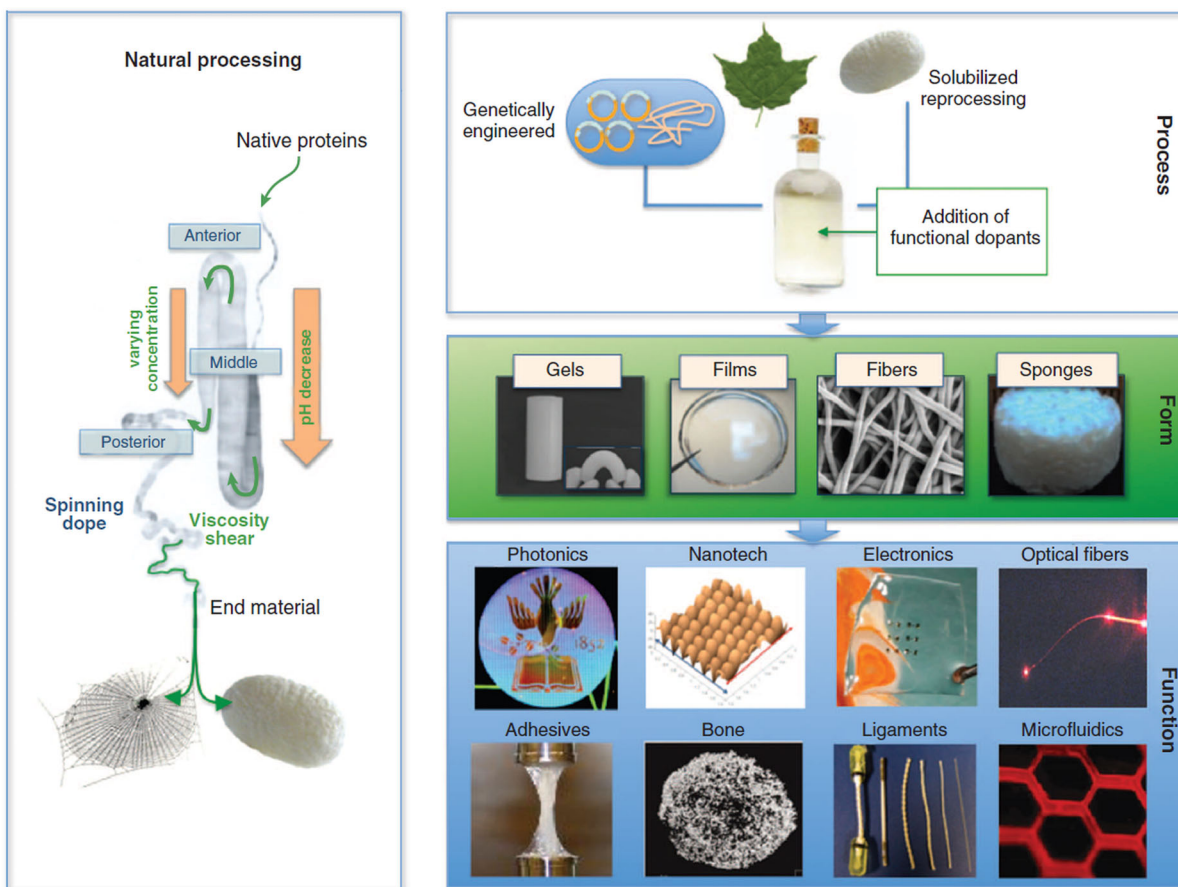


Figure 11. Generating new materials and opening new applications for silks. Left: native silk processing. Top right: engineered silk production starting from either reconstituted native silk proteins or genetically engineered silks. A wide range of materials and various applications (bottom right) can be generated from silks through processing into hydrogels, fibers, sponges, films and many other forms (middle right). Reproduced with permission from Ref. 61.

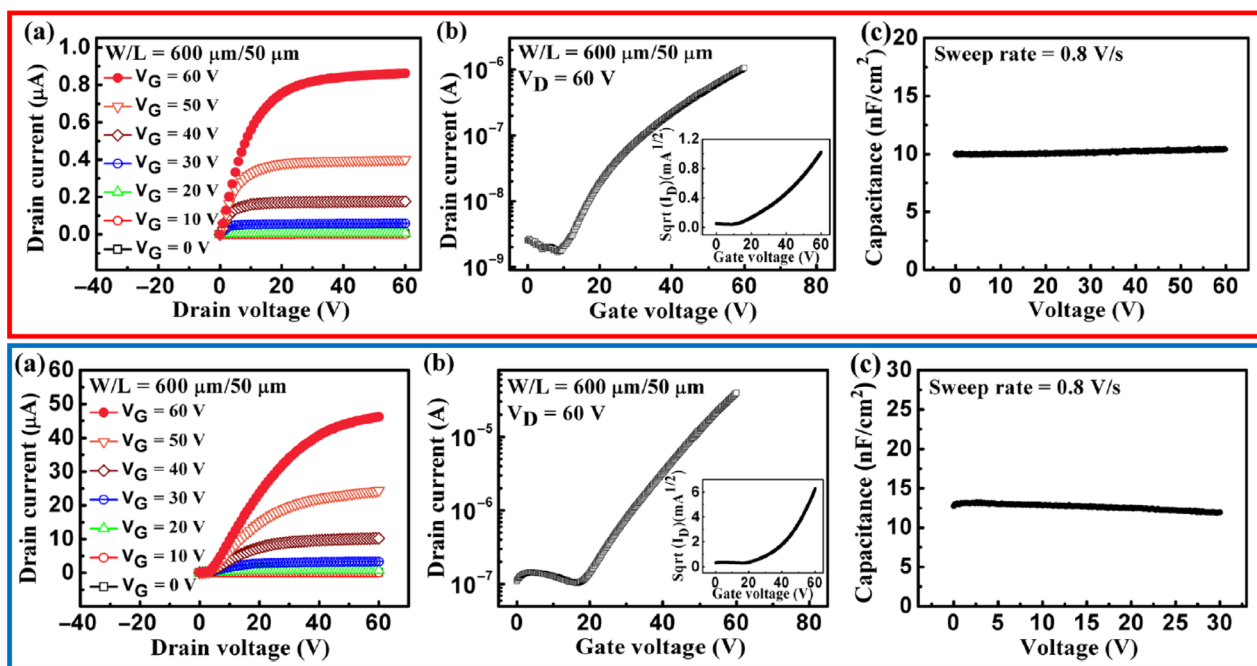


Figure 12. Electrical characteristics of fullerene C_{60} semiconductor on (red frame) Au gate electrode–silk dielectric and (blue frame) Au gate electrode–silk dielectric with 2 nm of pentacene as interlayer to favor the growth of larger C_{60} crystallites. (a) Output characteristics; (b) transfer characteristics; (c) quasi-static capacitance versus voltage curve recorded at a sweep rate of 0.8 V s^{-1} . Reproduced with permission from Ref. 64.

involving activated carbon and even hypochlorite bleaching. A schematic of the production process of shellac is presented in Fig. 13.

The three main constituents forming the complex structure of Shellac are aleuritic, jalaric and shellolic acids, presented in Fig. 14; however, the full list of components comprises more than 40 chemicals.^{74,75}

Among the constituents, resins sum up to *ca* 70–85% of the total weight, waxes *ca* 3–8% and various other molecules *ca* 5–10% of shellac. The hydrophobic nature of shellac is mainly imparted by aleuritic acid, but the wax content adds to the water-repelling and barrier properties of shellac too. For hydrophobicity purposes, wax-containing shellac is theoretically better than wax-free shellac; in addition, waxes also help in rendering shellac a better film-formation property since they interfere with different substrates and impact the adherence with the substrate. Hence dewaxed versions are generally the formulations typically offered to customers, and waxes are added separately depending on the type of target applications. Fresh shellac is easily soluble in various alcohols; however, water solubility is possible only in weakly alkaline solutions. Stability of shellac is negatively impacted if stored for more than 2 years at temperatures above 20 °C, since it undergoes a slow polymerization and esterification reaction between the carboxyl and hydroxyl groups of two neighboring component molecules (see Fig. 14). As a consequence of this reaction, both the hydrophobicity of shellac and its solubility in alcohol solution diminishes. Therefore, extreme care must be taken when ordering shellac from chemical suppliers, especially when the age of shellac and the storage conditions are unknown or not reported; in general, storing shellac at cold temperatures (refrigeration) ensures product stability.

Although the major applications of shellac are in the food and pharmaceutical industries,⁷⁶ given by its nontoxic, even edible characteristics, shellac has been reported recently also in various emerging technological fields, i.e. electronics and sensor fabrication,^{77–86} microfluidics^{87–89} and health monitoring devices.^{90–93} In one of the earliest demonstrations of shellac as dielectric for OFETs, commercially available, wax-containing shellac (obtained from the chemical supplier Sigma-Aldrich) was employed as gate dielectric for low-voltage-operating, hysteresis-free OFETs (Fig. 15, red panel) with both

pentacene (p-type) and C₆₀ (n-type) semiconductors. Shellac displays remarkable dielectric properties, demonstrated by a relatively flat capacitance over a measurement window of 8 orders of magnitude, from 10 kHz to 0.1 mHz, while having an outstanding breakdown field of *ca* 9 MV cm⁻¹ (Fig. 15, blue panel). All these accolades come in conjunction with an outstanding film-forming characteristic, exemplified in Fig. 15 (green panel), where a spin-coated film of shellac has a root-mean-square (r.m.s.) surface roughness of only 0.4 nm, while a drop-cast film of shellac has a surface roughness of *ca* 1 nm. Figure 15 (orange panel) presents the results of a recent study where a commercially available dewaxed shellac (obtained from the shellac producer AF Suter) was employed as a matrix for the embedment of inorganic nanoparticles, sepiolite, montmorillonite (MMT), vermiculate and halloysite with the end goal of creating thin films of high dielectric constant.⁷⁹ Due to its admirable film-forming characteristics and low interface trap density at the interface with the organic semiconductors pentacene and C₆₀, the OFETs with MMT and shellac as dielectric layer operate at low voltages of about 3 to 4 V, while exhibiting hysteresis-free behavior in

Shellac - Chemical Structure

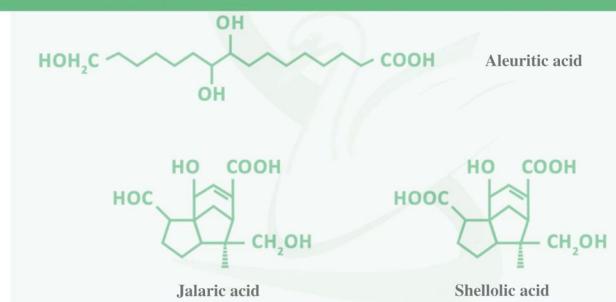


Figure 14. Three main constituents of shellac. The full composition of shellac includes more than 40 molecules, among them esters of aleuritic, jalaric, shellolic and butolic acids, as well as colorants and waxes. Drawing courtesy of Rahul Mourya, AF Suter Inc.

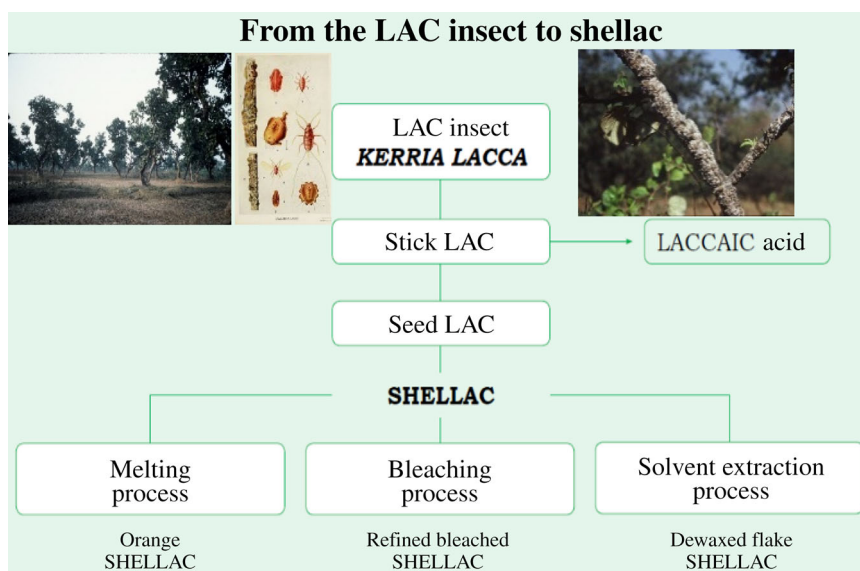


Figure 13. Schematic of shellac production. The insets show photographs the shellac plantations in forms of kusum trees and seedlac deposited on a tree branch. Courtesy of Rahul Mourya, AF Suter Inc.

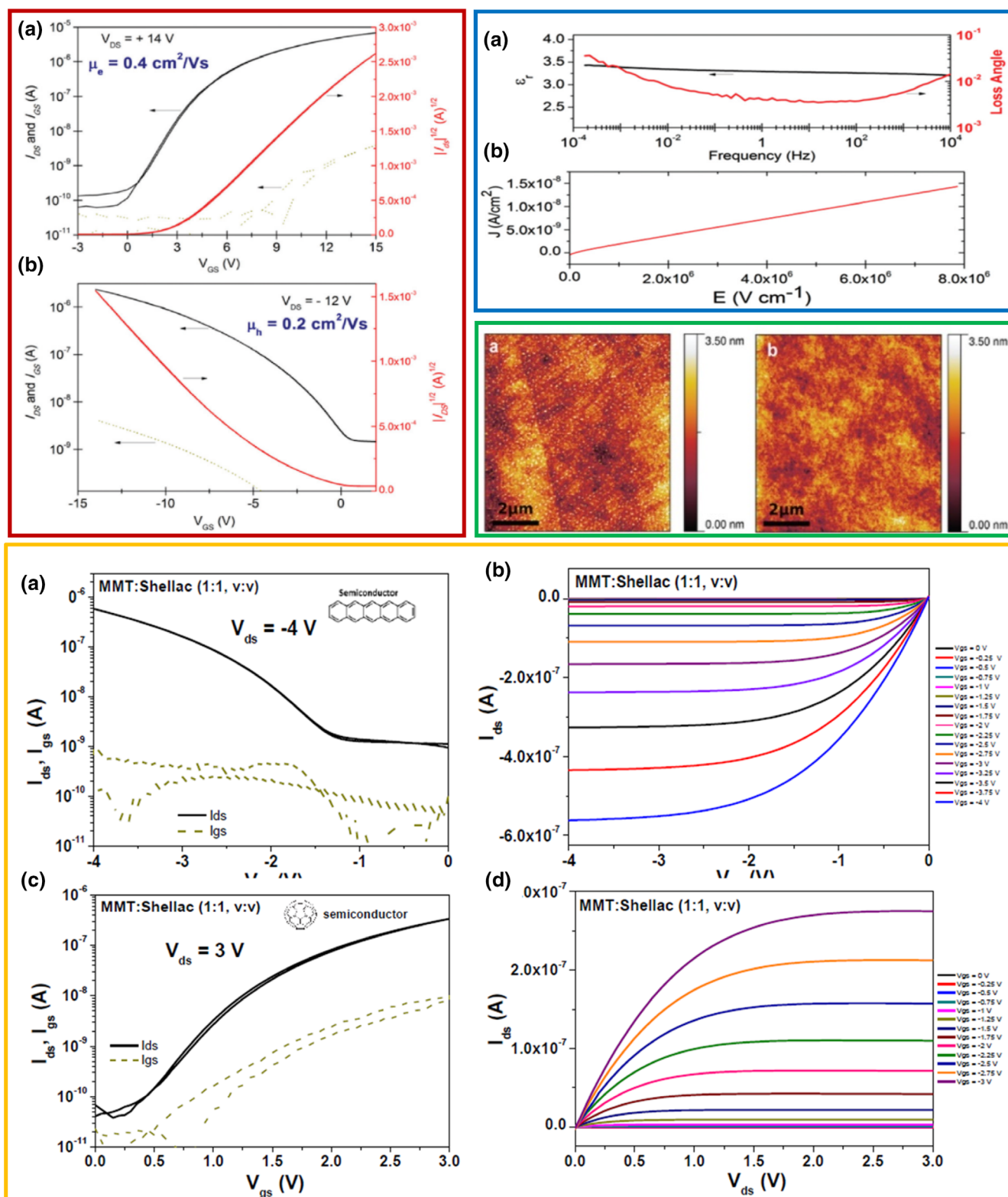


Figure 15. Red panel: (a) Transfer characteristics of fullerene C_{60} OFET using shellac as both a substrate and dielectric layer. (b) Transfer characteristics for a similar structure with pentacene semiconductor. Blue panel: Electrical measurements of metal-insulator-metal structures with shellac sandwiched between top and bottom aluminium electrodes. (a) Relative permittivity and loss angle as a function of probing; (b) J - E characteristics for a 150 nm spin-coated film of shellac that has breakdown field as high as 9 MV cm⁻¹. Green panel: AFM images of shellac deposited via: (a) drop-casting, resulting in a 0.5 μm thick shellac film, r.m.s. roughness ca 1 nm; and (b) spin-coating, resulting in a 30 nm shellac film, r.m.s. roughness ca 0.4 nm. Reproduced with permission from Ref. 77. Orange panel: Transfer and output characteristics of OFET devices with clay-shellac homogeneous mixture as gate dielectrics and (a, b) pentacene semiconductor and (c, d) fullerene C_{60} semiconductor. The dielectric constant of various mixtures of shellac and MMT spanned between 5.3 and 7.7, depending on the intake of MMT nanoparticles. Reproduced with permission from Ref. 79.

both transfer and output characteristics. The study also demonstrates that shellac can be successfully employed as a matrix for many inorganic fillers of high dielectric constant. In the particular case of the study cited, the dielectric constant of shellac film was basically doubled, increasing from a typical value of *ca* 3–4 for a pure shellac film to a value of *ca* 7.5–7.7 for shellac films containing inorganic nanoparticles sepiolite and MMT.

CONCLUSIONS

Natural polymers represent a viable basis for the establishment of biodegradable, eco-friendly plastic products with applicability in wide range of domains. In this respect, innovation in the sense of finding new markets and functionalities for biopolymers represents an integral aspect of industrial development. Known since ancient times, cellulose and lignin as biopolymers of plant origin and shellac and silk as biopolymers of animal origin are opening new industrial horizons for markets that complement those occupied by traditional, petroleum-derived plastic products. Their abundance translates to low cost of the base materials; their versatility and appealing eco-friendly and low-toxicity features guarantee the continued interest of the scientific community in developing new products and highlighting new functionalities. Thus, the utilization of these natural polymers in emerging applications like electronics and sensor development has been presented in this article, demonstrating that these biopolymers possess optimum characteristics that can assist in the development of high-performance, eco-friendly and sustainable products.

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